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Removal of Lead (II) from Aqueous Solutions by Biosorption on Brown Seaweed, *Sargassum Baccularia*

Mahmoud, A.Barah[1] Ibrahim, S. Shaban[2] Khairy, M. Al-Amari[3] Karima, A. Yahia[1]

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Authors affiliation
[1]Marine biology research centre,Tajura-Libya.
[2] Environmental chemistry, Libyan Academy,Janzour-Libya.
[3] Environmental science, Libyan Academy,Janzour-Libya
mahbarah@yahoo.com

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ABSTRACT

The purpose of this work is to investigate the batch removal of Pb^{2+} from aqueous solutions using marine dried brown seaweed *S. baccularia*. Seaweed was used as a low-cost adsorbent. The effects of pH, contact time, temperature, shaking speed and the concentration of the Pb^{2+} solution were examined in the biosorption process with S. baccularia. The results showed that when S. baccularia was used as the bioadsorbent, the optimum pH, Pb^{2+} concentration, equilibrium time, temperature, and shaking speed were 3, 20 ppm, 120 min, 30°C, and 120rpm. The equilibrium adsorption data are fitted to the Langmuir isotherm model. The separation factor (R_L) in the experiment was less than one (<1), indicating that the adsorption of metal ions on *Sargassum baccularia* adsorbent is favorable. The calculated activation energy (*Ea*) implies that the adsorption of Pb (II) on brown seaweed is a physical adsorption. Thermodynamic results show that adsorption occurs spontaneously in nature.

إزالة ايونات الرصاص من المحاليل المائية بواسطة الامتزاز الحيوى للعشب البحرى البنى *Sargassum baccularia*

محمود عبدالمطلب باره.إبراهيم سالم شعبان.خيرى محمد العمارى. كريمه عبدالله يحي

كان الهدف من هذا العمل إزالة أيونات معدن الرصاص من المحاليل المائية باستخدام العشب البحرى البنى *Sargassum baccularia* المجفف حيث استخدم هذا العشب كمادة مازه غير مكلفه.تمت دراسة تأثير بعض العوامل فى عملية الامتزاز مثل الاس الهيدروجينى، درجة الحرارة، زمن التلامس، سرعة الاهتزاز، التركيز الاولى للمعدن.اظهرت النتائج ان افضل امتزاز لايونات المعدن حدث عند درجة الحموضه 3.0 ووقت الاتزان عند 120 دقيقه ودرجة الحراره عند 30 درجه مئويه وسرعة اهتزاز 120 دوره فى الدقيقه وتركيز اولى للمعدن 20 جزء فى المليون.البيانات المتحصل عليها من الامتزاز عند حدوث التوازن كانت مناسبه لنموذج لونغمير، كان معامل الفصل (R_L) في التجربة أقل من واحد (<1) ، مما يشير إلى أن امتزاز أيونات المعادن على الماده المازه *Sargassum baccularia* تكون ملائمه لعملية الامتزاز. تشير طاقة التنشيط المحسوبة (*Ea*) إلى أن امتزاز ايونات الرصاص (II) بواسطة العشب البحري البني هو امتزاز فيزيائى. اظهرت النتائج الديناميكية الحرارية أن الامتزاز يحدث تلقائيًا.

INTRODUCTION

Heavy metal levels in the environment that are too high can harm living organisms. The majority of lead concentrations found in the environment are result of human activity. Lead can enter the environment through a variety of sources, including lead smelting, battery manufacturing, paper and pulp, boat and ship fuels, printing presses, automobile exhaust, paints and varnishes, metal products, and cables and pipelines. One of the metals with the most harmful effects on human health is divalent lead Pb (II) (Oubagaranadin and Murthy,2009). The removal and recovery of heavy metals from wastewater is critical for environmental and human health protection (Vimala and Das,2009). Heavy metals can be removed from wastewater using a variety of techniques, such as: precipitation, electrolysis, flocculation, crystallization, adsorption, chemical precipitation etc. However, these technologies often demand high initial and maintenance costs, have low inefficiency (especially at low concentrations), offer no regeneration, need large amount of chemicals, generate new types of pollutants etc(Seolatto *et al*.,2014). As a result, there is a constant need to search for an optimal technology while taking into account its cost, materials used, and efficiency (Farooq *et al*.,2010). Biosorption, which is based on biological materials' ability to remove and accumulate heavy metals from aqueous solutions, has received a lot of attention in recent years due to some advantages over traditional techniques (Esmaeili *et al*.,2015). Absorbent materials (biosorbents) derived from appropriate biomass can be used to effectively remove and recover heavy metallic ions from wastewater streams (Saravanan *et al*.,2011). Brown macroalgae were indicated as potential materials for metal removal among the examined adsorbents because they have high metal binding capabilities, are a renewable biological resource, and are available in large quantities (Al prol *et al*.,2019). The cell wall of the brown algae contains considerable amounts of polysaccharides such as alginates, fucoidans in addition to acid functional groups as acetamido, hydroxyl, amino, carbonyl, amino and amido (Vieira and Volesky,2000). Functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals (Sarı and Tuzen,2008) .*Sargassum sp*., brown seaweed composed primarily of the polysaccharide alginate, commonly calcium and sodium alginates, has a significant propensity for heavy metal accumulation when compared to other algae genera (Da Costa *et al*.,2001). The purpose of this study was to evaluate the efficacy of *Sargassum baccularia* as an adsorbent for the removal of cadmium ions from aqueous solutions by investigating the effect of various variables (pH, temperature, contact time, shaking speed, and initial metal concentration) on the biosorption process.

MATERIALS AND METHODS

BIOMASS

Brown seaweed *Sargassum baccularia*. Will be used in this work is harvested from the sea (Northwestern Coast of Libya). Initially washing the seaweed biomass with tap water to remove the impurities and sand, and finally with distilled water to remove salt and particulate material from its surface. Drying washed biomass at 60ºC for 24 hours. The biomass was crushed after being dried with mortar and pestle, then the samples were sieved. The samples will be first sieved through a 200 µm mesh, and then through a 63 µm mesh. The milled particles with 63 µm will be used for sorption experiments. Drying milled biomass at 105ºC for 24 hours to calculate the dry weight.

METAL SOLUTIONS

The concentration of metal solution was prepared by 1.0 g/l metal (1000 ppm) using atomic absorption spectroscopy standard Fluka.

BIOSORPTION EXPERIMENTS

The batch experiment was conducted out in 250 ml flasks containing the required quantity of algal biomass (1.0 g) and 50 ml of each metal solution. For each solution, different initial pH (2.0 to 6.0) and temperature range (20°C to 40°C) were used. The flasks were placed in a shaker with constant shaking at 0 to 120 rpm for different time intervals of 30, 60, 120, 180, 240,300 and 360 min. After the requested time interval, the biomass was separated by filtering the content using Whatman No.40 filter paper. The quantity of metal adsorbed on the adsorbent was calculated from the variance between the metal concentration in the solution before and after the biosorption process. Concentration of metal in the solution after the equilibrium was determined using a Perkin Elmer Analyst 400 flame absorption spectrometer.

EFFECT OF PH

Biosorption experiments were performed at different pH ranges from 2.0 to 6.0. Effect of pH was carried out with *Sargassum baccularia* biomass as biosorbent. The experiment was carried out using the required *Sargassum baccularia* biomass in 50 ml of 5, 10 and 20 ppm metal solution. The optimum pH that gives the maximum removal of metals from this study was determined. NaOH and H_2SO_4 solutions are used to adjust pH. The binding sites were not available due to competition between metal and H^+ ions when pH was below 2.0, therefore pH values below 2.0 were not followed.

EFFECT OF TEMPERATURE

The biosorption experiment was set up with a different temperature range from 20 to 40 °C, using 50 ml of metal stock solution.

EFFECT OF CONTACT TIME

In order to study the effect of time on the biosorption process, the contact time ranged from 30 to 360 min using the desired biomass in 50 ml of metal solution adjusted to the appropriate pH. Samples were removed every 1 hour interval and filtered and analyzed for metal concentration on Perkin Elmer Analyst 400 flame absorption spectrometer.

EFFECT OF SHAKING SPEED

The biosorption experiment was performed at different shaking speeds ranging from 0 to 120 rpm for the metal solution.

DATA EVALUATION

The metal adsorption (q) and bioremoval efficiency (R) with *Sargassum baccularia* were calculated using the following formulae.

$$\mathbf{q} = \frac{(C_i - C_f)\ V}{M} \qquad \textbf{(1)}$$

$$\textbf{Removal}(\%) = \frac{(C_i - C_f)}{C_i} \times \mathbf{100} \qquad \textbf{(2)}$$

Where q =metal adsorption (mg/g); M= dry mass of Sargassum baccularia (g); V = volume of initial metal solution used (ml); R = bioremoval efficiency (%); C_i = initial concentration of metal in aquatic solution (mg/L); C_f = final concentration of metal in aquatic solution (mg/L) (Ok *et al*.,2007).

EQUILIBRIUM STUDIES

Adsorption isotherms describe the distribution of adsorbate molecules between liquid phases at different equilibrium concentrations. Finding a suitable model that fits the adsorption data yields important insights into the adsorption process, such as how the interaction between adsorbent and adsorbate occurs. The most widely used adsorption models are the Langmuir and Freundlich equations. (Alnajrani and Alsager,2020). Langmuir equation, which is valid for monolayer sorption onto a surface, with homogeneous sites was given by Eq. 3.

$$\mathbf{q} = \mathbf{q}_{max} \frac{bC_f}{1 + bC_f} \qquad \textbf{(3)}$$

Where q_{max}(mg/g) is the maximum amount of the metal ion per unit weights of seaweed to form a complete monolayer on the surface bound at high C_f(mg/L), and b is a constant related to the affinity of the binding sites(mg/L),q_{max} represents a practical limiting adsorption capacity when the surface is fully covered with metal ions and assists in the comparison of adsorption performance(Chatterjee *et al* .,2010). The qmax and b can be determined from the liner plot of C_f/q versus C_f.

The basic features of the Langmuir adsorption model may be expressed in terms of a dimensionless constant called a separation factor (R_L) that is defined by the following equation (4).

$$\mathbf{R_L} = \frac{1}{1 + bC_f} \qquad \textbf{(4)}$$

Value of R_L indicates the nature of the sorption process. When R_L value lies between 0 and 1 then adsorption is favourable,

If R_L is > 1 adsorption is unfavorable,
If R_L is =1 adsorption is linear,
If R_L is = 0 adsorption is irreversible

The empirical Freundlich equation based on sorption on a heterogeneous surface is given below by Eq. 5.

$$\mathbf{q = K\ C_f}^{(1/n)} \qquad \textbf{(5)}$$

The k and n parameters are the constants of the Freundlich isotherm. n is an empirical parameter, which varies with the degree of heterogeneity and K is related to biosorption capacity (Lodeiro *et al*.,2006). For a good absorbent, 0.2< 1/n< 0.8, and a smaller value of 1/n shows better adsorption and formation of a rather strong bond between the adsorbate and the absorbent (Esmaeili *et al*.,2015).

RESULTS AND DISCUSSION

EFFECT OF INITIAL PH

The biosorption of metal ions onto biosorbents is a pH-dependent process (Tuzun *et al*.,2005). When evaluating the sorption capacity of an adsorbent ions sequestering from aqueous solution, pH is one of the most significant parameter to consider. Because of its impact on the surface properties of the adsorbent and the ionic forms of the metal in solution, the pH of the system controls the sorption capacity (Memon *et al*.2008). The pH range for Pb (II) biosorption was selected 2 to 6 because the majority of industrial wastewater containing heavy metals is acidic (Parekh *et al*.,2016).Figure 1 depicts the effect of pH on the biosorption of Pb (II) by brown seaweed. The results showed that the maximum lead uptake was at pH 3, and the minimum uptake was at pH 2, the lead uptake decreased after pH 3. According to (Waghmode and Sabale,2013), the decreased rate of biosorption at higher pH may be due to a decrease in metal solubility, which causes complexes to form and precipitation. Lead will precipitate in the form of metal hydroxides at pH value > 5.5 (Nessim *et al*.,2011). Many types of low-soluble hydroxyls are formed at high pH, such as: $Pb\ (OH)^{+}$, $Pb\ (OH)_2$ and $Pb(OH)^{3-}$ (Matei,2011; Abdel-Ghani and El-Chaghaby,2014; Morosanu *et al*.,2017). Precipitation reduces the rate of biosorption by immobilizing metal ions so that ions are not available for biosorption (Matei,2011). It has been suggested that at pH 2, the functional groups are positively charged due to the high concentration of protons (H^+), which increases the competition of protons for the same sites of active sites (binding sites) that metals can use, resulting in a reduction in the absorption of metal ions on the biomass surface(Rahman and Sathasivam,2016). At low pH values the biomass

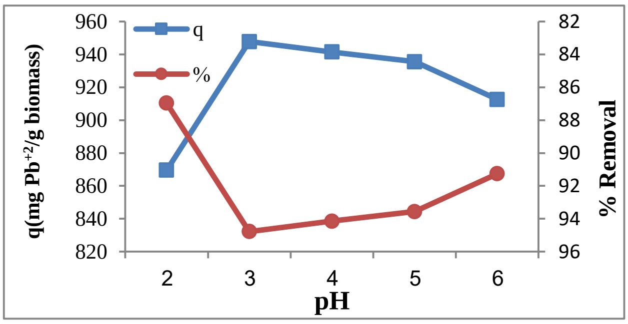


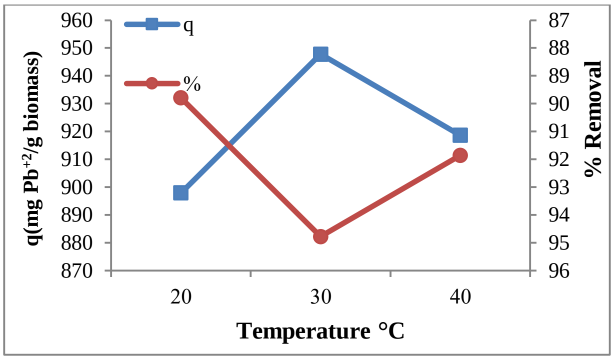
Fig (1): Effect of pH on Pb (II) removal at 20 mg/l, T = 30°C, t= 360min, 1g biomass.

surface, would be closely connected to (H3O$^+$) that restricts the access of the metal ions to the functional groups of surface (Jnr and Spiff, 2004).

EFFECT OF TEMPERATURE:

From the results shown in Figure (2), biosorption capacity increased with increasing temperature in the 20-30°C interval, where the highest metal uptake (q) value was found at 30°C, while biosorption capacity decreases with increasing temperature in the 30-40°C interval. The lowest metal uptake (q) was found at 20°C. (Parekh et al.,2016), reported that the removal of lead by dried biomass of brown algae, *Sargassum*, maximum sorption was found at 25 °C and it was suggested that biomass changes its properties at high temperatures due to denaturation. Adsorption decreased as temperature increased due to decreased surface activity. (Aksu and Tezer,2000). The reason for the decrease in surface activity is the decay of active regions on the biosorbent's surface at higher temperatures or bond breaking, suggested by (Uzunoglu *et al*.,2014). Furthermore, it has been reported that the attractive forces between the biomass surface and the adsorbate are weak at high temperatures and thus the metal uptake (q) decreases (Jnr and Spiff,2005). Metal uptake has been observed to generally increase with temperature over a certain range (e.g. 20-35°C) but decreases with temperature above the critical value, thus biosorption processes are usually performed at temperatures between 5 and 35°C (Pingxin,2005). The present study also revealed the same thing, as the biosorption capacity decreased at an increasing temperature, 30°C was chosen as the optimum temperature at which the maximum uptake (q) occurred.

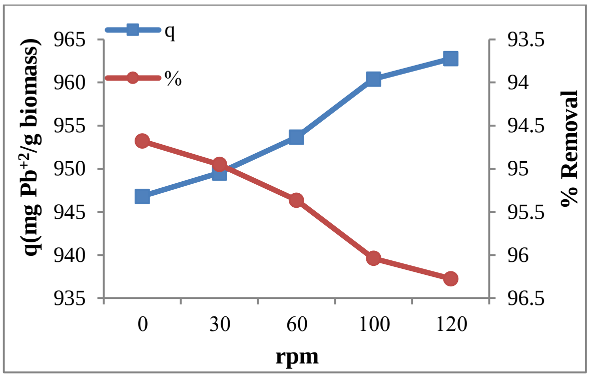
Fig (2): Effect of Temperature on Pb (II) removal at pH3, 20 ppm, 1g biomass, t=360min



EFFECT OF CONTACT TIME:

Contact time is the time necessary for the biosorption process to be equilibrium when no major changes in biosorption capacity are observed after a certain period of time. As shown in Figure (3) the metal uptake was 899.3 mg/g (89.93%) through the first 30 min and then the metal uptake increased slowly and was equilibrium after 120 min. After two hours, the time increase did not improve the metal uptake rate. According to (Sheng *et al*.,2004) for the impact of contact time on biosorption, two stages of kinetic behavior are evident, with very rapid initial adsorption occurring within a few minutes, followed by a long interval of much slower uptake (especially in the case of *Sargassum* – metal and *Padina* – metal systems), the equilibrium time needed for the various metal-biomass systems ranged from about 1 to 3 hrs, so it was considered in subsequent experiments that the contact time of (6 hrs) was more than sufficient to establish the equilibrium. It has been suggested that the initial rapid phase may involve an ion exchange mechanism or a physical adsorption mechanism on the cell surface, and that the subsequent slower stage may involve another mechanisms such as: micro-precipitation, complexation or saturation of active sites (binding sites) (Jayakumar *et al*.,2014). (Sheng *et al*.,2007), reported that the all adsorption equilibrium was attained within 3 h, 90% of the total adsorbed metal ions occurred within 10-60 min by *Sargassum sp*, and therefore 6 h was sufficient for the equilibrium experiments. It has been suggested that, in the initial stage, there are many vacant sites (binding sites) on the biomass surface and, after a period of time, it becomes difficult to occupy the remaining vacant sites (binding sites) due to the repulsive forces occurring between the solute molecules (metals) on the biomass surface and the bulk phase (Kannan *et al*.,2010). After two hours, there were no important changes in the capacity of biosorption. However, the experimental data were measured for 6 hours to ensure complete equilibrium. In this work, a contact time of 2 hours was chosen for subsequent experiments.

Fig (3): Effect of contact time on Pb (II) removal at pH=3, 20ppm, T= 30°C, 1g biomass.



EFFECT OF SHAKING SPEED

Figure (4) shows the impact of varying shaking speeds on Pb (II) ion biosorption. The results showed an increase in metal uptake with an increase in shaking speed. The maximum metal uptake was at 120 rpm, while the minimum uptake was at 0.0 rpm. These results can confirm that the raise in shaking speed increases the diffusion of lead ions to the seaweed surface (Antunes *et al*.,2003). Lead biosorption by seaweed in the range (50–250 rpm) was sufficient to ensure that all binding sites are readily available for metal uptake by minimizing film thickness, shaking reduces the thickness of the film and eventually eliminates film resistance (Nessim *et al*.,2011). It has been found that the increased shaking speed (high speed) leads to reduced biosorption capacity, due to random collisions between molecules (adsorbate-adsorbate, adsorbent-adsorbate, and adsorbent-adsorbent) do not provide sufficient time for heavy metal ion to bind with the active sites (binding sites) on the adsorbent(biomass) surface(Raza *et al*.,2015). Interaction between aqueous and solid phases was more effective at moderate speeds (Marandi *et al*.,2010). At low shaking speed, the adsorbent accumulated in the metal solution instead of the diffusion, where the adsorption is carried out by the active sites in the upper layer of the adsorbent, while the active sites in the lower layer buried are not available, so the removal only takes place on the upper layer, therefore the shaking rate should be appropriate, so that all the active sites are available to uptake the metals (Rehman *et al*.,2015). Reducing the shaking speed of the biomass leads to cost savings in the industrial scopes (WillIams and Edyvean,1997). In this work, 120 rpm was selected as the optimum shaking speed at which the maximum metal uptake was at 120 rpm.

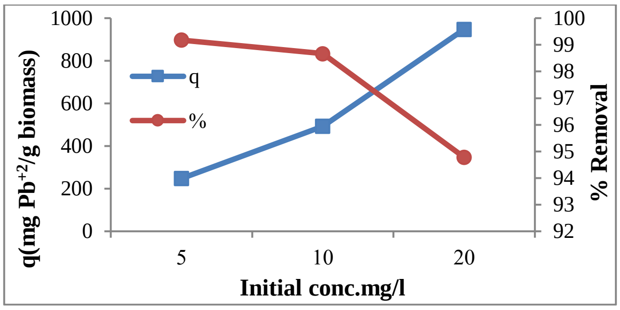


Fig (4): Effect of shaking speed on Pb (II) removal by S.baccularia at pH=3, 20ppm, t=120min, 30°C, 1g biomass.

EFFECT OF INITIAL METAL ION CONCENTRATION

The initial metal concentration is a significant factor affecting the biosorption process, as this factor gives the driving force to beat all mass transfer resistances between the liquid and the solid phases (Esmaeili *et al*.,2015). The effect of the initial metal concentration on the removal of Pb (II) was achieved by differing the initial concentration from 5 mg/l to 20 mg/l per 50 ml of metal solution, 1 g biomass at pH 3 and 360 minute contact time, the graph was plotted between the initial concentration and the metal removal percentage as appear in Figure (5), the biosorption capacity of Pb (II) was observed as (247.95 mg / g) 99.18% for 5 mg/l and (947.8 mg / g) 94.78 % for 20 mg/l. The results appeared that the quantity of adsorbed lead increased with a rise in the initial concentration, while the metal removal percentage decreased with a rise in the initial concentration. High initial concentrations contain a great quantity of metal ions available for adsorption. Initial metal concentrations provide a driving force to beat the resistances of the mass transfer between the solid and liquid phases (Pirbazari *et al*.,2014). The metal removal percentage decreases when the initial concentration increases, at a specific metal concentration, all metal ion binding sites (active sites) on the adsorbent surface (biomass) are saturated, equilibrium establishment between the biomass and the adsorbate Al-Homaidan *et al*.,2014). When the initial concentration of metal increases, the collisions between the adsorbent (active sites) and the metal ions increase, consequently, the metal uptake increases (Vasanthi *et al*.,2010). In this work, 20 mg/l was chosen, as the highest metal uptake occurred at this concentration.

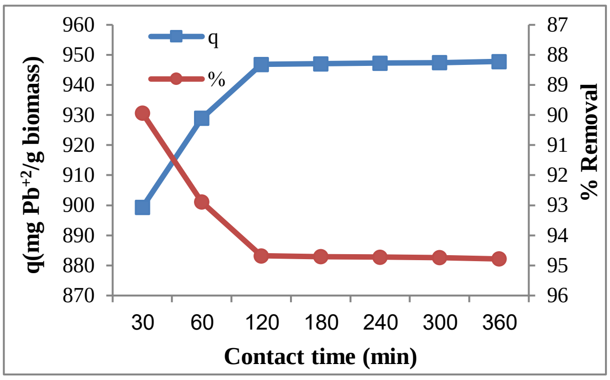


Fig (5): Effect of initial concentration on Pb (II)removal by *S.baccularia*, H=3,T=30°C,1g biomass.

ADSORPTION ISOTHERMS

When the adsorption process reaches an equilibrium state, the adsorption isotherm shows how the adsorbed molecules distribute between the liquid and solid phases. Figure 6 presents the plot of amount of Pb (II) adsorbed against its concentration in aqueous phase at equilibrium. The amount of lead adsorbed increased when the initial lead concentration was raised from 5.0 to 20.0 mg/l, according to isotherm data obtained with a range of initial lead concentrations. The adsorption data was analyzed using two adsorption models that used the Langmuir and Freundlich isotherm equations.

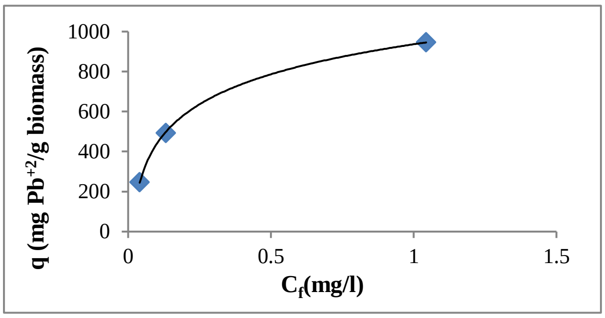


Fig.6. Adsorption isotherm for Pb (II) on S.baccularia at 30°C, pH=3, t=360min, 1g biomass.

LANGMUIR MODEL

The quantity of R_L in Sargassum baccularia was 0.096 - 0.714, which is consistent with the requirement for favorable adsorption. The high correlation coefficient, R^2, indicated better coordination between the parameters and monolayer adsorption of Pb (II) ions onto the biosorbent surface (Fig. 7).

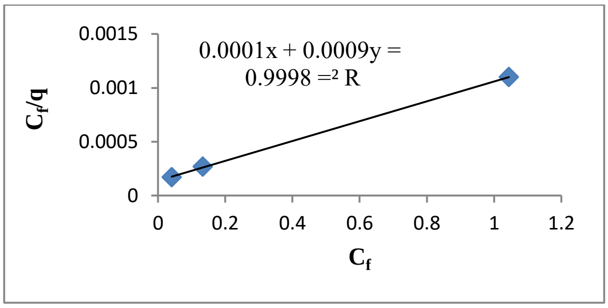


Fig (7): Langmuir isotherm for adsorption of Pb (II) on *S. baccularia* at 30°C, pH=3, t=360min, 1g biomass

THE FREUNDLICH MODEL

The values of K and n obtained in this work are shown in Table 2. The correlation coefficient, R^2, values in this case indicated that the Freundlich model was less well fitted to the experimental data than the Langmuir equation (Fig. 8).

Table. 1. Langmuir and Freundlich constants for the adsorption of Pb (II) ions by brown seaweeds.

Seaweed	Langmuir constant		
S.baccularia	q_{max}(mg/g)	b(l/mg)	R^2
	1111	9.01	0.9998

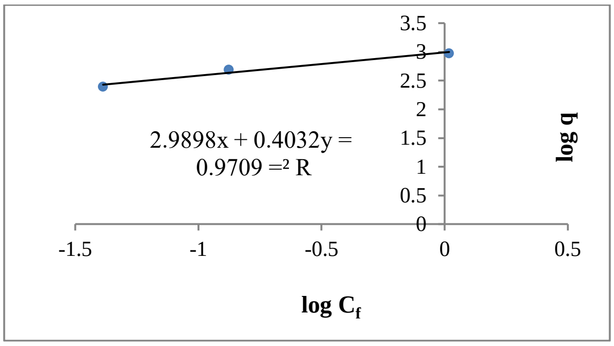


Fig (8): Freundlich isotherm for adsorption of Pb (II) at T= 30°C, pH=3, t=360min, 1g biomass

Table. 2. Freundlich constants for the adsorption of Pb (II) ions by brown seaweeds

Seaweed	Freundlich constant		
S.baccularia	K(mg/g)	n	R^2
	976.8	2.5	0.9709

ADSORPTION THERMODYNAMICS MODELING

Thermodynamic parameters for adsorption of metal onto biomass were calculated using the following equations:

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

$$\Delta G = -RT \ln k_d \qquad (7)$$

Because K_d is equilibrium constant, its dependence on temperature can be used to estimate both the enthalpy change (ΔH) and the entropy change (ΔS) associated with the biosorption process:

$$\ln k_d = \frac{-\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (8)$$

$$k_d = \frac{q_e}{C_f} \qquad (9)$$

Where R is the universal gas constant (8.314 J/mol K), T the temperature (K), and k_d (q_e/C_f) is the distribution coefficient. q_e is the adsorption capacity ($mg.g^{-1}$), C_f ($mg.L^{-1}$) is the concentration of metal at equilibrium ($mg.L^{-1}$).

The plot of ln K_d as a function of 1/T yielded a straight line from which a ΔH value equal to 10.04 (kJ/mol) and a ΔS value equal to 86.4 (J/molk) were calculated.

Table 3.Thermodynamic parameters for the adsorption of Pb on brown seaweed (*Sargassum baccularia*)

Metal	**Δ*H*(kJ/mol)**	**ΔS(J/molk)**	**ΔG (kJ/mol) at different temperatures**		
			293.15k	**303.15k**	**313.15k**
Pb^{+2}	**10.04**	**86.4**	**-15.17**	**-16.03**	**-16.93**

Enthalpy change data can be used to distinguish between physisorption and chemisorption. Physisorption is typically associated with adsorption heats ranging from 2.1 to 20.9 kJ/mol (0.5 to 5 kcal/mol), whereas chemisorption is associated with much larger ΔH values ranging from 20.9 to 418.4 kJ/mol (5 to 100 kcal/mol) (Li *et al.*,2010). The enthalpy result of brown seaweed is in the first range (2.1 to 20.9 kJ/mol), which suggests that adsorption of metals on brown seaweed is a physisorption process. These results are consistent with the activation energy (*Ea*) calculated using the Arrhenius equation (10).

$$\ln(k_{ads}) = \ln(A) - \frac{E_a}{RT} \qquad (10)$$

The magnitude of activation energy gives an idea about the type of adsorption, which is mainly physical or chemical. Low activation energies (5 to 40 kJ/mol) are characteristics for physisorption, while higher activation energies (40 to 800 kJ/mol) suggest chemisorption (Li *et al.*,2010; Nollet *et al.*,2003). The calculated activation energy (*Ea*) for biomass was 0.797J/molk for Pb, this activation energy is characteristic for a physical adsorption.

Table 4.Activation energy for the adsorption of Pb on brown seaweed (Sargassum baccularia)

Metal	Ea(J/molk)
Cd	0.797

CONCLUSION

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to support resident populations of moths Species richness and abundance., Thus, these relict forests are serving to foster persistence of moths species across a landscape matrix that is largely devoid of suitable habitat. It is evident that public parks and gardens would not replace large forest reserves due to their relative smaller sizes., We, therefore, strongly recommend that an integrated approach to forest and Natural Reserves management and conservation work should be adopted in this area.

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